

## CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

# The Thermodynamic Properties of Nitrogen, Argon, Oxygen, and Their Mixtures in the Region of the Liquid–Gas Phase Transition

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**Abstract**—A procedure for constructing the equation of state for metastable and labile regions in the liquid–gas phase transition is suggested. A consistent description of  $p$ ,  $\rho$ ,  $T$ , and caloric properties was obtained. The spinodals of both pure fluids and their mixtures were located.

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Much work has been done to study the thermodynamic properties of nitrogen, argon, and oxygen. A wealth of experimental data have been collected, which contributed to the construction of quite a number of unified equations of state describing the regions of the gas and liquid phases simultaneously. The most accurate unified equations of state suggested in [1–4] were recognized as reference quality equations [5]. These equations are written as expansions of the Helmholtz energy in temperature and density and take into account experimental data on  $p$ ,  $\rho$ , and  $T$  and the caloric properties of fluids. In addition to single-phase state parameters, they allow liquid–vapor phase equilibrium parameters, critical point positions, the second and third virial coefficients, etc., to be determined. At the same time, the isotherms of these unified equations exhibit oscillations in labile regions, and pressure oscillations are as large as  $\sim 10^{20}$  MPa [6]. For instance, for argon, a decrease in the temperature from critical ( $T_c = 150.687$  K) to 145 K results in the appearance of positive  $(\partial p / \partial \rho)_T$  derivative values on isotherms in the labile region. A monotonic decrease in the pressure as the density increases would be physically correct. The reason for satisfying this condition is at least twofold. First, the unified equations of state of pure fluids is a basis for constructing unified equations of multicomponent systems [1, 7], which presupposes the use of the extended law of corresponding states in the form

$$\frac{a(T, \rho, \mathbf{x})}{RT} = \alpha(T, \rho, \mathbf{x}) \quad (1)$$

$$= \sum_{i=1} x_i [\alpha_i^0(T, \rho) + \alpha_i^r(\tau, \delta) + RT \ln x_i] + \alpha^E(\tau, \delta, \mathbf{x}).$$

Here,  $\alpha$  is the Helmholtz energy per mole of the substance,  $R$  is the universal gas constant,  $T$  is the temper-

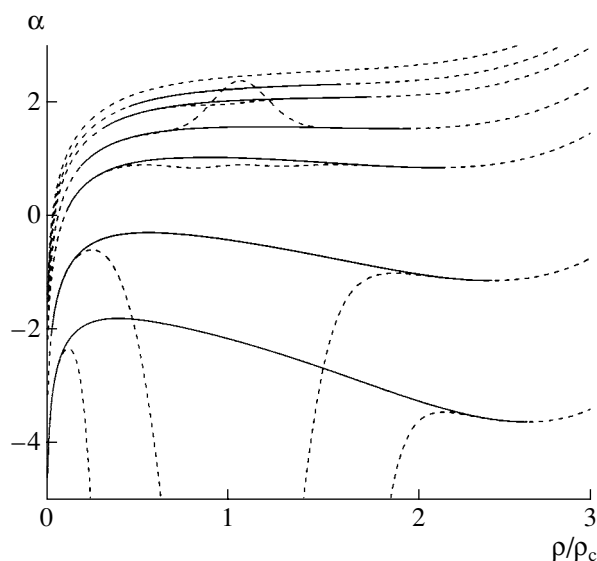
ature,  $\rho$  is the density,  $\mathbf{x}$  is the set of the concentrations of separate components,  $\alpha_i^r$  is the configurational part of the Helmholtz energy,  $\tau = T_r(\mathbf{x})/T$ ,  $\delta = \rho/\rho_r(\mathbf{x})$ ,  $\alpha^E$  is the correction for nonadditivity, and  $\alpha^0$  is the ideal gas contribution to the Helmholtz energy. The  $T_r(\mathbf{x})$  and  $\rho_r(\mathbf{x})$  reduction parameters are as a rule quadratic functions of concentration. Equation (1) does not rule out situations when the mixture is stable at  $\tau$  and  $\delta$  values that correspond to a metastable or even labile region for one or several its components. For instance, according to the equation of state from [7], phase equilibrium in an oxygen–argon solution at 85 K and argon concentration in the liquid phase  $x_{\text{Ar, liq}} \approx 90\%$  is attained at the liquid phase density that corresponds to the metastable state of pure oxygen at a pressure of  $\approx -13$  MPa. The second reason is related to the development of continual approaches to describing the properties of liquid–gas interfaces [8, 9]. For instance, it follows from the molecular dynamics experiments [9] that the density of a substance is described by a smooth function of the spatial coordinate in the liquid–gas transition, and the characterization of the state of fluids in the interphase layer requires obtaining an equation that correctly describes metastable and labile regions.

The “smoothness” of isotherms in the phase transition region is attained in this work by means of approximating the Helmholtz energy  $\alpha$  by the equation

$$\alpha = \alpha_0 - \frac{\alpha_1}{\omega} + \frac{\alpha_2}{t} \ln \omega + \frac{\alpha_3}{t} \omega$$

$$+ \frac{\alpha_4 \omega^2}{t} \frac{1}{2} + \frac{\alpha_5 \omega^3}{t} \frac{1}{3} + \frac{\alpha_6 \omega^4}{t} \frac{1}{4} + \frac{\alpha_7 \omega^5}{t} \frac{1}{5}, \quad (2)$$

where  $\omega = \rho/\rho_c$  and  $t = T/T_c$ . For pressure, this leads to a polynomial sixth-order in density,

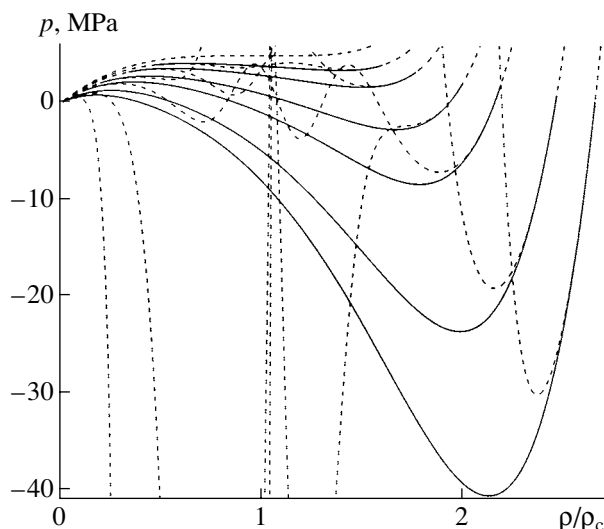


**Fig. 1.** Reduced Helmholtz energy  $\alpha = a/RT$  of argon along the isotherms (from top to bottom)  $T = T_c$ , 145, 140, 130, 120, 100, and  $T_{tr} = 83.8058$  K. The isotherms were constructed according to the unified equation from [2] (dashed lines) and approximation polynomial (2) (solid lines).

$$p/\rho_c RT_c = t\omega^2 \alpha_\omega = a_1 t + a_2 \omega + a_3 \omega^2 + a_4 \omega^3 + a_5 \omega^4 + a_6 \omega^5 + a_7 \omega^6. \quad (3)$$

The  $a_i$  coefficients in (2) and (3) are functions of the temperature. At a given temperature, the  $a_1$ – $a_7$  values are found by solving the seven equations

$$p(\rho') = p_s, \quad p(\rho'') = p_s, \quad \left(\frac{\partial p}{\partial \rho}\right)_{T, \rho=\rho'} = p'_p, \quad \left(\frac{\partial p}{\partial \rho}\right)_{T, \rho=\rho''} = p''_p, \quad (4)$$



**Fig. 2.** Argon pressure isotherms. See Fig. 1 for notation.

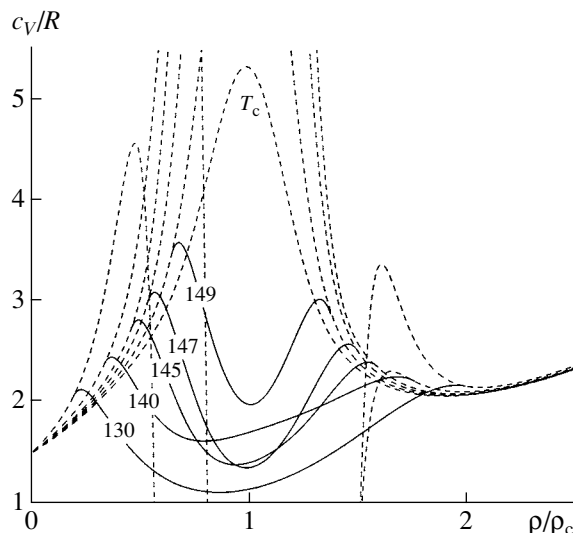
$$\left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T, \rho=\rho'} = p'_{pp}, \quad \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T, \rho=\rho''} = p''_{pp}, \quad \int_{\rho''}^{\rho'} \frac{p}{\rho^2} d\rho = p_s \left(\frac{1}{\rho''} - \frac{1}{\rho'}\right), \quad (5)$$

where (5) is the Maxwell rule of equal areas. The orthobaric densities  $\rho'$  and  $\rho''$ , saturation pressure  $p_s$ , and first  $p_p$  and second  $p_{pp}$  derivatives in the liquid (one prime) and gas (two primes) states are determined according to the reference equations of state [1–5]. The remaining coefficient ( $a_0$ ) is found from the Helmholtz energy along the saturation line, that is, using either of the two conditions

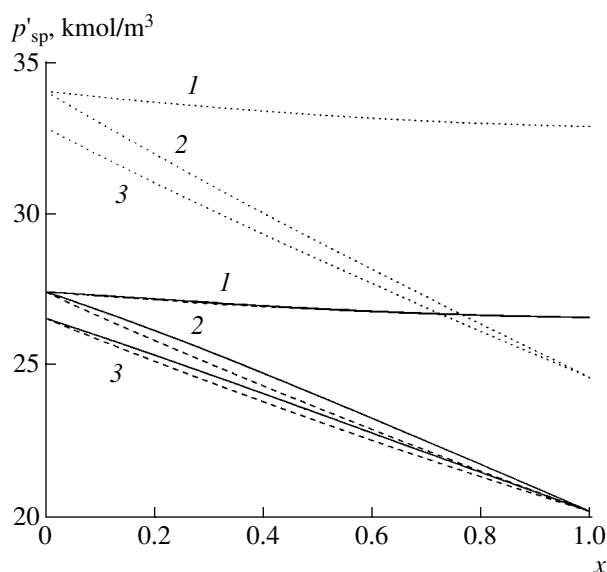
$$\alpha(\rho') = \alpha', \quad \alpha(\rho'') = \alpha''. \quad (6)$$

If Maxwell rule (5) is satisfied, both conditions (6) are met simultaneously. The  $a_0, a_1, \dots, a_7$  coefficients can also be determined without recourse to (5) by solving the system of eight equations (4), (6). Conditions (6) then become independent, and pressure (3) automatically satisfies Maxwell rule (5). It follows that polynomial (2) is stiffly bound up with the reference equation on a binodal, as concerns both the Helmholtz energy value and its derivatives with respect to density up to the third order.

The  $\alpha(T, \rho)$  energy surface  $\pi$  determined by (2) in the vicinity of the liquid–gas phase transition exhibits physically correct behavior and smoothly sews stable gas and liquid regions together (see Fig. 1). For nitrogen and argon, the procedure described above is applicable at temperatures from critical  $T_c$  down to the triple point  $T_{tr}$ , and for oxygen, down to the  $\approx 0.5 T_c$  temperature. The pressure isotherms have the classic van der Waals form even at the lowest temperatures (Fig. 2),



**Fig. 3.** Isochoric heat capacity of argon along isotherms.



**Fig. 4.** Liquid densities along binary solution spinodals  $p'_{sp}$  depending on the concentration of the second component: (1)  $O_2 + Ar$ , (2)  $O_2 + N_2$ , and (3)  $Ar + N_2$ . Diffusion (11) and mechanical (9) spinodals are shown by solid and dashed lines, respectively. Dotted lines correspond to liquid densities along binodals  $\rho'_s$ .  $T = 100$  K.

which allows us to reliably estimate the positions of the liquid and gas spinodals. The heat capacity isotherms  $c_v(\rho)$  (Fig. 3) contain a fairly sharp minimum immediately below the critical isotherm as a compensation of a sort for the presence of the critical maximum. This minimum decreases as the temperature lowers and changes into a maximum in the vicinity of the triple point. As pressure  $p(T, \rho)$  (3) and heat capacity

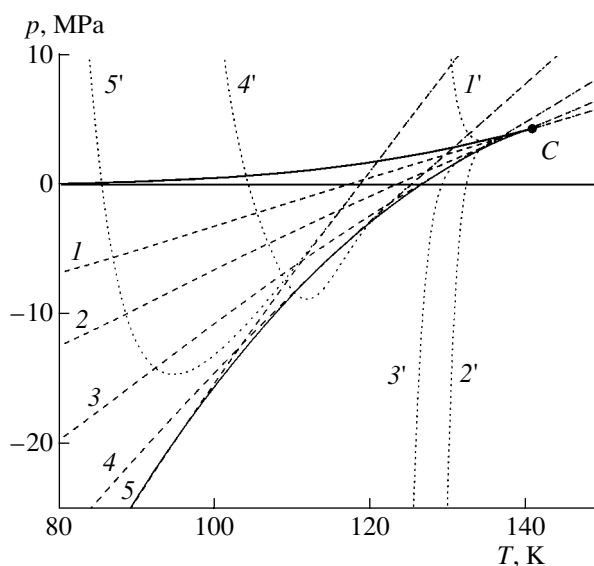
$$c_v(T, \rho) = -R \left[ t^2 \left( \frac{\partial^2 \alpha}{\partial t^2} \right)_w + 2t \left( \frac{\partial \alpha}{\partial t} \right)_w \right] \quad (7)$$

surfaces are determined as partial derivatives of unified fundamental equation of state (2), they satisfy the well known identity

$$T \left( \frac{\partial^2 p}{\partial T^2} \right)_\rho = -\rho^2 \left( \frac{\partial c_v}{\partial \rho} \right)_T, \quad (8)$$

that is, are mutually consistent.

The rules of mixing for  $T_r(\mathbf{x})$  and  $\rho_r(\mathbf{x})$  and the equation for the nonadditive contribution  $\alpha^E(\delta, \tau, \mathbf{x})$  obtained in [7] allow the procedure for sewing together the reference unified equations of states of pure substances (see above) to be used for describing the thermodynamic properties of their solutions in the region of the liquid–gas phase transition. The pressure isotherms of the  $N_2 + O_2 + Ar$  ternary system and the  $O_2 + Ar$ ,  $O_2 + N_2$ , and  $Ar + N_2$  binary solutions along constant



**Fig. 5.** Phase diagram of the equimolar solution  $O_2 + N_2$  ( $x = 0.5$ ) in the pressure–temperature coordinates. Solution isochores at  $p/p_c = (1) 1.0$ , (2) 1.25, (3) 1.5, (4) 1.75, and (5) 2.0 are shown by dashed lines, and the same isochores calculated by the equation of state for solutions from [7], by dotted lines. Solid lines correspond to the binodal and diffusion spinodal, and  $C$  is the critical point.

composition lines are similar to the isotherms of the pure substances (Fig. 2). The condition

$$\left( \frac{\partial p}{\partial \rho} \right)_{T, x} = 0 \quad (9)$$

determines the mechanical spinodal of the solution. The diffusion spinodal is reached when the stability determinant vanishes,

$$(\mu_1, \mu_2, \dots)/(\rho_1, \rho_2, \dots)|_T = 0. \quad (10)$$

For binary solutions, this gives

$$\left( \frac{\partial(\mu_1 - \mu_2)}{\partial x} \right)_{p, T} = 0. \quad (11)$$

Calculations show that the differences between the mechanical and diffusion spinodals of gases and liquids in binary solutions of nitrogen, oxygen, and argon are negligibly small. The only exception is density values along the liquid-phase spinodal of nitrogen-containing solutions (Fig. 4).

The phase diagram of the equimolar  $N_2 + O_2$  solution is shown in Fig. 5 in the pressure–temperature coordinates. Isochores in metastable and labile regions are virtually rectilinear continuations of isochores in stable regions. The spinodal of the liquid is close to the line of extrema (9) enveloping the family of isochores. For comparison, the same figure contains isochores of this solution obtained using the unified equation of state from [7]. Because of their nonphysical behavior in the labile and metastable regions, not only diffusion spinodal (11) calculations but also enveloping curve (9) construction become impracticable. In metastable liquid solution regions, substantial differences between the isochores constructed by the equation from [7] and those deter-

mined by the sewing procedure (Eqs. (2)–(6)) at low temperatures begin with negative pressures approximately two times lower in magnitude than the limiting extensions corresponding to the spinodals. It follows that the suggested procedure for describing the thermodynamic properties of pure fluids and their solutions may be necessary for analyzing and interpreting experimental data on cavitation in strongly extended liquids.

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